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(11)

**EP 1 013 797 A1**

(12)

**EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
28.06.2000 Bulletin 2000/26

(51) Int Cl.7: **C23G 1/10**, F01D 5/00,  
F01D 25/00, C23G 1/00

(21) Application number: **99310313.4**

(22) Date of filing: **21.12.1999**

(84) Designated Contracting States:  
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE**  
Designated Extension States:  
**AL LT LV MK RO SI**

(30) Priority: **22.12.1998 US 219153**

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(54) **Method of removing hot corrosion products from a diffusion aluminide coating**

(57) A method of removing hot corrosion products from the surface of a component exposed to corrosive conditions at elevated temperatures, as is the case with turbine, combustor or augmentor components of gas turbine engines. The method is particularly suited for the removal of hot corrosion products from components protected with a diffusion aluminide coating, either as an environmental coating or as a bond coat for a thermal barrier coating (TBC). The processing steps of the meth-

od include immersing the component in a heated liquid solution containing acetic acid, and then agitating the surfaces of the component while the component remains immersed in the solution. In this manner, hot corrosion products on the surfaces of the component are removed without damaging or removing the diffusion aluminide coating. As a result, regions of the component from which the hot corrosion products were removed can then be repaired by a suitable aluminizing process.

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## Description

[0001] This invention relates to methods for repairing gas turbine engine components protected by diffusion aluminide coatings. More particularly, this invention is directed to a process by which hot corrosion products are removed from a diffusion aluminide coating without damaging the coating, and therefore enables the coating to be rejuvenated instead of being completely removed and replaced.

[0002] The operating environment within a gas turbine engine is both thermally and chemically hostile. Significant advances in high temperature alloys have been achieved through the formulation of iron, nickel and cobalt-base superalloys, though components formed from such alloys often cannot withstand long service exposures if located in certain sections of a gas turbine engine, such as the turbine, combustor and augmentor. A common solution is to protect the surfaces of such components with an environmental coating, i.e., a coating that is resistant to oxidation and hot corrosion. Coatings that have found wide use for this purpose include diffusion aluminide coatings and overlay coatings such as MCrAlY (where M is iron, nickel and/or cobalt), which may be overcoated with a diffused aluminide coating. During high temperature exposure in air, these coatings form a protective aluminum oxide (alumina) scale that inhibits oxidation of the coating and the underlying substrate. Diffusion aluminide coatings are particularly useful for providing environmental protection to components equipped with internal cooling passages, such as high pressure turbine blades, because aluminides are able to provide environmental protection without significantly reducing the cross-sections of the cooling passages. As known in the art, diffusion aluminide coatings are the result of a reaction with an aluminum-containing composition at the component surface. The reaction forms two distinct zones, an outermost of which is termed an additive layer that contains the environmentally-resistant intermetallic phase MA1, where M is iron, nickel or cobalt, depending on the substrate material. Beneath the additive layer is a diffusion zone containing various intermetallic and metastable phases that form during the coating reaction as a result of diffusional gradients and changes in elemental solubility in the local region of the substrate.

[0003] Hot corrosion of gas turbine engine components generally occurs when sulfur and sodium react during combustion to form sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), which condenses on and subsequently attacks the components' surfaces. Sources of sulfur and sodium for hot corrosion reactions include impurities in the fuel being combusted as well as the intake of sodium laden dust and/or ingestion of sea salt. In the latter situation, hot corrosion typically occurs on hot section turbine blades and vanes under conditions where salt deposits on the component surface as a solid or liquid. The salt deposits can break down the protective alumina scale on the alu-

minide coating, resulting in rapid attack of the coating. Hot corrosion produces a loosely adherent external scale with various internal oxides and sulfides penetrating below the external scale. These products are generally sulfur and sodium compounds with elements present in the alloy and possibly other elements from the environment, such as calcium, magnesium, chlorine, etc. As such, hot corrosion products are distinguishable from oxides that normally form or are deposited on gas turbine engine components as a result of the oxidizing environment to which they are exposed.

[0004] Traditionally, aluminide coatings have been completely removed to allow component repair by welding or brazing or to replace damaged coating, after which a new aluminide coating is applied by any suitable aluminizing process. Any hot corrosion products present in the coating are removed with the coating. A disadvantage of completely removing an aluminide coating from a gas turbine engine component is that a portion of the substrate metal is removed with the coating, which significantly shortens the useful life of the component. As a result, new repair technologies have been proposed by which diffusion aluminide coatings are not removed, but instead are rejuvenated to restore the aluminide coating and the environmental protection provided by such coatings. However, coating rejuvenation technologies for turbine blade and vane repair cannot be performed in the presence of hot corrosion products, since any remaining hot corrosion products would result in attack of the rejuvenated coating upon exposure to engine temperatures. Because hot corrosion products have required removal by abrasive grit blasting, rejuvenation technologies have been limited to components that have not been attacked by hot corrosion.

[0005] From the above, it can be appreciated that, in order to successfully implement a rejuvenation program for turbine engine components having diffusion aluminide coatings that are exposed to sea salt and other sources of sulfur and sodium, hot corrosion products must be removed without damaging the aluminide coatings. Treatments with caustic solutions in autoclaves have been successfully used to remove oxides of aluminum and nickel from components, but such treatments have not been successful at removing hot corrosion products for the apparent reason that the more complex hot corrosion products are not soluble in caustic solutions. Accordingly, the prior art lacks a process by which hot corrosion products can be completely removed without damaging or removing a diffusion aluminide coating.

[0006] The present invention provides a method suitable for removing hot corrosion products from the surface of a component exposed to salt solutions and other sources of sodium and sulfur at extremely high temperatures, as is the case with turbine, combustor or augmentor components of gas turbine engines. The method is particularly suited for the removal of hot corrosion

products from components protected with a diffusion aluminide coating, either as an environmental coating or as a bond coat for a thermal barrier coating (TBC).

**[0007]** The processing steps of a particular embodiment of this invention generally include conditioning or activating the surface to be cleaned by processing through caustic autoclave and/or grit blasting operations, immersing the component in a heated liquid solution containing acetic acid, and then agitating the surfaces of the component while the component remains immersed in the solution. In this manner, it has been determined that hot corrosion products on the surfaces of the component are removed without damaging or removing the diffusion aluminide coating. As a result, regions of the component from which the hot corrosion products were removed can then be repaired by a suitable rejuvenating process. If desired, the component can be pretreated by autoclaving with a caustic solution to remove oxides from the surface of the component. Such an autoclaving treatment can be followed by water jet stripping to remove a TBC (if any) adhered to the component with the aluminide coating.

**[0008]** Weak acetic acid solutions such as white vinegar have been unexpectedly found to remove hot corrosion products if used at certain temperatures and supplemented with sufficient agitation following a surface conditioning or activation step. Advantageously, such weak acetic acid solutions have been found not to attack aluminide coatings, permitting rejuvenation of an aluminide coating instead of complete removal of the coating and then application of a new coating. Another advantage of this invention is that acetic acid does not foul wastewater treatment facilities, and can be disposed of without concern for exceeding allowable levels for metal ion concentrations in wastewater. Accordingly, the treatment of this invention is environmentally friendly.

**[0009]** Other objects and advantages of this invention will be better appreciated from the following detailed description.

**[0010]** One embodiment of the present invention provides an uncomplicated and environmentally safe method for removing hot corrosion products contained within aluminide coatings on the surfaces of gas turbine engine components subjected at high temperatures to sources of sodium and sulfur, including fuels, dust and sea water. Notable examples of such components include the high and low pressure turbine nozzles and blades, shrouds, combustor liners and augmentor hardware of gas turbine engines. Of particular interest to the invention are gas turbine engine components protected with a diffusion aluminide coating or a MCrAlY coating overcoated with a diffused aluminide coating, which may or may not be accompanied by a ceramic topcoat as a TBC. While the advantages of this invention will be described with reference to gas turbine engine components, the invention is generally applicable to any component having an aluminized surface that would benefit from being rejuvenated without removal of the existing aluminide coat-

ing.

**[0011]** The method of this invention entails treating an aluminized surface attacked by hot corrosion with a weak acetic acid solution, an example of which is white vinegar typically containing about 4 to 8 weight percent acetic acid. While copending and commonly-assigned U. S. Patent Application Serial No. 09/009,236 to Bowden discloses that vinegar has been found to remove dirt and silica and calcium-based compounds from gas turbine engine components, the ability of vinegar and other weak acetic acid solutions to remove complex hot corrosion products chemically bonded to an aluminide coating was unknown and unexpected. According to this invention, a weak acetic acid solution in combination with a suitable surface pretreatment has been surprisingly determined to completely remove hot corrosion products without damaging or removing those portions of the coating that have not been attacked by hot corrosion. While vinegar is generally preferred as the treatment solution of this invention due to availability and cost, it is foreseeable that stronger and weaker acetic acid solutions derived by other methods could be used.

**[0012]** The process of this invention preferably entails processing a component through a suitable surface pretreatment, immersing the component in an acetic acid solution at about 150°F to about 175°F (about 66°C to about 79°C), though temperatures between about 120°F and 200°F (about 49°C and about 93°C) are believed to be suitable. While different solution strengths are possible, preferred acetic acid concentrations for the solution are about 4% to about 5%. Complete immersion of the component ensures that all surfaces, including any internal surfaces such as those formed by cooling passages, are contacted by the solution. The surfaces of the component are then agitated, such as by ultrasonic energy, to dislodge the hot corrosion products from the component surfaces. Suitable parameters for an ultrasonic cleaning operation can be readily ascertainable by those skilled in the art, with shorter durations being possible when the component is subjected to higher ultrasonic energy levels. Generally, a two-hour duration using a commercially-available ultrasonic cleaner has been found to be sufficient to remove a majority of the hot corrosion products chemically bonded to an aluminide coating. A preferred treatment is about two to about four hours to ensure complete removal of hot corrosion products. Following ultrasonic cleaning, the component is rinsed with water or another suitable rinse to remove the acetic acid solution from the internal and external surfaces of the component. The component is then ready for rejuvenation of its aluminide coating by any suitable aluminizing process. During rejuvenation, diffusion aluminide is redeposited on those regions from which hot corrosion products were removed. Prior to rejuvenation, these regions are characterized by the absence of the additive layer of the original aluminide coating, though the diffusion zone remains.

**[0013]** The investigation leading to this invention in-

volved the treatment of high pressure turbine blades protected with diffusion aluminide environmental coatings that had been attacked by hot corrosion, which appeared as a blue-gray coloration on the surfaces of the blades. Each blade was first pretreated by autoclaving at between 150°C and 250°C and a pressure of between 100 and 3000 psi (about 0.7 to about 21 MPa) with a caustic solution containing sodium hydroxide. While autoclaving successfully dissolved engine oxides from the blades, hot corrosion products remained firmly adhered to the aluminide coatings, particularly on the concave surfaces of the blades. The turbine blades were then immersed tip-down in a container of undiluted white vinegar at a temperature of about 65°C (about 150°F). The container and blades were then subjected to ultrasonic agitation for a total of two hours, after which the blades were rinsed with tap water.

[0014] After the above treatment, and without any additional processing (e.g., grit blasting or tumbling), it was observed that the blue-gray colored hot corrosion product had been completely removed from two of the three blades. The hot corrosion product was completely removed from the third blade by light grit blasting that did not damage the aluminide coating on the blade surface. Metallurgical examination of the blades showed that the heated vinegar solution had reacted with and completely removed the corrosion product, which had been present in the additive layer of the coating. Importantly, the vinegar solution did not attack those uncorroded regions of the coating immediately adjacent those regions from which hot corrosion products were removed. As a result, the blades were in condition for rejuvenation of their aluminide coatings.

[0015] Following the success of the above results, additional testing was performed on a second group of high pressure turbine blades whose diffusion aluminide environmental coatings had been similarly attacked by hot corrosion. Instead of an autoclave pretreatment, each blade was first pretreated by grit blasting to clean the surfaces of the blades. These blades were also immersed tip-down in a container of undiluted white vinegar at a temperature of about 65°C (about 150°F), subjected to ultrasonic agitation for a total of two hours, and then rinsed with tap water. Inspection of the blades after rinsing showed that the hot corrosion product had been completely removed from all of the blades.

[0016] From the above results, it was concluded that vinegar and other weak acetic acid solutions can be used to clean and remove hot corrosion products and oxides from aluminized surfaces without damaging the aluminide coating. It was further concluded that treatment with the weak acetic acid solution is best carried out with a caustic autoclave process or grit blasting as a surface conditioning or activation pretreatment to enhance the removal of oxides of the type that form as a result of the oxidizing operating environment within a gas turbine engine. Suitable autoclaving conditions are believed to include the use of sodium hydroxide as the

caustic solution using conventional autoclaving pressures and temperatures. In addition, it was concluded that the acetic acid treatment of this invention can be used in conjunction with caustic autoclave stripping to first remove a ceramic TBC on a diffusion aluminide coating (in which case, the coating serves as a bond coat for the TBC), and then remove hot corrosion products from the exposed aluminide coating. This latter procedure can also include water, jet stripping the TBC in accordance with U.S. Patent Application Serial No. (Attorneys' Docket No. 13DV-12550), which is incorporated herein by reference.

[0017] While the invention has been described in terms of a preferred embodiment, it is apparent that other forms could be adopted by one skilled in the art. For example, suitable acetic acid solutions could contain other constituents, both inert and active.

## Claims

1. A method for removing hot corrosion products from the surface of a gas turbine engine component protected by a diffusion aluminide coating, the method comprising the steps of:
  - immersing the component in a liquid solution containing acetic acid; and then
  - agitating the surface of the component while immersed in the solution so that the hot corrosion products on the surface of the component are removed without damaging or removing the diffusion aluminide coating.
2. A method as recited in claim 1, further comprising the step of aluminizing the surface of the component to repair regions of the surface from which the hot corrosion products were removed.
3. A method as recited in claim 2, further comprising the step of rinsing the solution from the surface of the component prior to the aluminizing step.
4. A method as recited in any preceding claim, wherein the component is immersed in the solution for at least two hours.
5. A method as recited in any preceding claim, wherein the solution is maintained at about 150°F to about 175°F during the agitation step.
6. A method as recited in any preceding claim, wherein the agitation step is performed by subjecting the component to ultrasonic energy.
7. A method as recited in any preceding claim, further comprising the step of, prior to the immersion step, subjecting the component to a caustic solution at a

pressure of about 100 psi to about 3000 psi and at a temperature of about 150°C to about 250°C to remove oxides from the surface of the component.

8. A method as recited in claim 7, wherein a ceramic coating overlies the diffusion aluminide coating on the surface of the component, the method further comprising the step of, following the step of subjecting the component to the caustic solution but prior to the immersion step, subjecting the component to water jet stripping to remove the ceramic coating from the component. 5 10
9. A method as recited in any preceding claim, further comprising the step of, prior to the immersion step, grit blasting the surface of the component. 15
10. A method as recited in any preceding claim, wherein all hot corrosion products on the surface of the component are removed during the agitation step. 20
11. A method as recited in any preceding claim, wherein the component is a turbine blade. 25

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# EUROPEAN SEARCH REPORT

Application Number  
EP 99 31 0313

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	US 3 607 398 A (LUCAS JOSEPH G) 11 May 1971 (1971-05-11) * claim 1 *	1	C23G1/10 F01D5/00 F01D25/00 C23G1/00
A	FR 2 483 963 A (GEN ELECTRIC) 11 December 1981 (1981-12-11) * claims 1,5 *	1,7	
A	US 4 439 241 A (AULT EARLE A ET AL) 27 March 1984 (1984-03-27) * column 2, line 22 - column 3, line 60 *	1,7	
D,P, A	US 5 938 855 A (BOWDEN JR JOSEPH H) 17 August 1999 (1999-08-17) * claim 1 *	1	
A	EP 0 165 104 A (SNECMA) 18 December 1985 (1985-12-18) * claims 1,2 *	1	
A	FR 2 560 893 A (SNECMA) 13 September 1985 (1985-09-13) * claim 1 *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.7)  C23G F01D C23F
A	US 4 119 437 A (ARENDT RONALD H ET AL) 10 October 1978 (1978-10-10)		
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>3 Apr11 2000</b>	Examiner <b>Torfs, F</b>
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons  &amp; : member of the same patent family, corresponding document</p>			

EPO FORM 1503 (03/02) (P04001)

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 31 0313

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

03-04-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3607398 A	11-05-1971	NONE	
FR 2483963 A	11-12-1981	US 4317685 A	02-03-1982
		DE 3121833 A	04-03-1982
		IL 62598 A	30-09-1984
		IT 1137031 B	03-09-1986
		JP 1041710 B	07-09-1989
		JP 1557198 C	16-05-1990
		JP 57023073 A	06-02-1982
		NL 8102705 A,C	04-01-1982
US 4439241 A	27-03-1984	NONE	
US 5938855 A	17-08-1999	NONE	
EP 0165104 A	18-12-1985	FR 2564350 A	22-11-1985
		CA 1275871 A	06-11-1990
		IL 75059 A	31-08-1988
		US 4655383 A	07-04-1987
FR 2560893 A	13-09-1985	CA 1294856 A	28-01-1992
		EP 0159221 A	23-10-1985
		JP 1814388 C	18-01-1994
		JP 5024997 B	09-04-1993
		JP 61006287 A	11-01-1986
		US 4707191 A	17-11-1987
US 4119437 A	10-10-1978	NONE	

EPO FORM P469

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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